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Scanning tunneling microscopy and photoemission studies of self-organised Ag nanostructures on the N-modified Cu(001) surface

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ABSTRACT

There has been a strong interest in methods of creating nanometer scale structures and in particular forming one- and two-dimensional electron confinement structures. Self-organisation has been recognised as a promising way for growing large nanostructure domains with sufficiently regular size and spacing as required for the observation of quantum well states. We investigated the electronic properties and the morphology of Ag nanostructures on c(2 × 2)-N/Cu(001) surface. This system is an example of epitaxial growth confined on nanoscale regions due to the occurrence of an adsorbate induced reconstruction. Using a combination of Scanning Tunneling Microscopy and Angle Resolved Photoemission Spectroscopy techniques we were able to determine the morphology and the growth mode of Ag on N-modified Cu(001) surface and the occurrence of quantum size effects in the electron properties of Ag nanostripes and nanoislands, evidenced in the observation of quantum well states.

1. Introduction

The bottom-up approach in the design and realization of nanostructure assemblies is a well-established method in nanoscience, and still it presents some fascinating aspects: in particular, fabrication of 2-D self-organized patterns and their use for creating regular assemblies of dots, wires and stripes is one of the most interesting phenomena in physics and chemistry, also for technological application [1-12]. In particular, adsorption of atomic nitrogen on the Cu(001) surface is a very good example of self-organisation [13,14]: at N-coverage Θ_N below saturation (saturation occurs at $\Theta_N = 0.5$ ML) the adsorption results in fact in the formation of regular arrays of square N islands with c(2 × 2) internal periodicity that run parallel to the ⟨100⟩ azimuth. The size of the square islands does not depend on the N-coverage and is equal to about 5 × 5 nm^2. The spacing between islands along the array is given by one line of Cu atoms, while the spacing between the arrays is inversely proportional to the N coverage. This peculiar arrangement of the adsorbates leaves stripe-shaped domains of clean Cu having a regular width. It was found that this periodic arrangement is caused by difference of surface stress in the clean and nitrided domains, and their competition with the domain boundary energy [15,16]. The regular island morphology can be monitored with Scanning Tunneling Microscopy (STM) [13,14], with Low Energy Electron Diffraction (LEED) [17,18] and Surface X-ray Diffraction (SXRD), in the last two cases by directly observing four-fold satellite peaks which appears around the (10) diffraction spots [16,19]. When the N coverage reaches a value $\Theta_N = 0.5$ ML, the square islands coalesce, with formation of an almost continuous N layer, with some interruptions caused by trenches parallel to ⟨110⟩ directions, which have a width of few nanometers and a height of a single atomic layer [13,14]. More recently, ribbon-like nanopatterns were obtained in vicinal regions toward ⟨100⟩ directions, with formation of N islands of rectangular shapes [20]. The N-modified Cu surface exhibits also strong reactivity to atomic H exposure, with formation of NH species at the surface and, by increasing the amount of H dosage, with formation and desorption of ammonia [21].

STM experiments found out that when transition metals such as Cu, Fe, Ni, Ag, Co, Au are deposited on the N-modified Cu(001) surface, epitaxial growth at its initial stages occurs preferentially on the clean Cu stripes [1,22-27], rather than on the N-covered parts of the surface. Therefore metal particles and stripes can be grown on the clean Cu areas, but the evolution of the growth with the metal coverage depends strongly on the particular metal used. For instance, the origin of preferential growth of Fe islands on bare Cu(001) areas was assigned to inclusion of Fe atoms at very low Fe coverage stage. These inclusions

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worked as centers of nucleation for the growth of 2D Fe islands on top of the Cu bare surface areas. After the bare Cu areas are completely covered, the Fe nanostructured films extend over the N-covered patches. X-ray Absorption Fine Structures (XAFS) studies confirmed the preferential growth of Fe islands on the bare Cu surfaces for $\Theta_N < 0.5$ ML, with Fe arranged in fcc lattice [28-30], and with the presence of some disorder in the islands, with inhomogeneous lattice distortion caused by tetragonal expansion and the presence of surface atoms arranged in nano-martensitic phase. When Fe is adsorbed on saturated c(2 × 2)-N surface, XAFS data analysis are compatible with a geometry where the Fe atoms substitute the Cu atoms underneath the N layer. Fe-Cu bond length values are instead typical of Fe in a fcc site [30]. SXRD experiments on the same system were also performed; Crystal Truncation Rods (CTR) analysis substantially confirmed the results of XAFS [19]. Co and Fe nanostructured films on N-modified Cu (001) exhibited also interesting magnetic properties, as revealed by magneto-optical Kerr effect [31], dichroism in photoemission [32] and absorption [33].

Ag nanostructured films on N-modified Cu surfaces were investigated, for low Ag coverage, with STM, showing the possibility of creating single crystal Ag nanowires on sub-saturated c(2 × 2)-N/Cu (001). The Ag nanowires formed on the bare Cu areas between the arrays of N islands and are therefore aligned along the < 100 > direction, up to 4 atomic layers thick [1,34]. The growth of Ag on the bare Cu areas followed the same evolution as the formation of Ag ultrathin films on clean Cu(001), with formation for low coverage of a c (10 × 2) superstructure, followed by a simple pseudoexagonal overlayer structure [35].

On the other hand, the effect of reduced dimensionality on the electron properties of Ag ultrathin films shown itself in a spectacular way by the onset of quantum well states, observed with Angle Resolved Photoemission Spectroscopy (ARPES) and due essentially to the confinement of Ag electrons by the film-vacuum and film-substrate interface. The films were grown on a variety of single crystal surfaces, either metals or semiconductors [36-44]. Aim of this work is to investigate the effect of the N-induced nanopatterning of Cu(001) on the Ag electronic states, in particular, the effect of lateral confinement induced by N surface nanostructuring on the QW. The present study follows the morphology of the growth of Ag on the N modified Cu(001) surface by means of STM from the very early stages and up to 8 ML. The electronic structure of the Ag overlayer is studied by means of angular integrated photoemission spectroscopy (PES) and ARPES.

2. Experimental

The Cu(001) surface was cleaned by cycles of Ar sputtering at 1 keV ion impact energy and annealing at 550 °C. The cleanliness of the surface thus obtained was checked by LEED and PES and by STM where applicable. The N overlayer was prepared by sputtering the Cu(001) surface with N_2 at medium ion impact energy (500 eV) until the accumulated charge on the sample (i.e. the product of the sample drain current and the sputtering time) was of the order of 90 μC. Cross-check also with previous STM observations shown that with this dosage the N precoverage is about 0.25 ML. The N_2 sputtering was followed by prolonged annealing (at least one hour) of the sample at 350 °C. This procedure resulted in a sharp LEED and large domains of N islands arrays as revealed also by STM. The photoemission experiments were carried on VUV-Photoemission and APE beamlines, both at the synchrotron radiation laboratory of Elettra, Trieste, during two different runs. STM data were acquired in a chamber connected with the APE endstation.

The N-Cu(001) surface prior to Ag deposition was characterized by means of low energy electron diffraction (LEED) every time. This technique allows to detect the formation of long arrays of c(2 × 2)-N islands due to the presence of extra diffraction spots to be attributed to long periodic structures such as the islands arrays. [13,14,22]. Ag was evaporated at room temperature from an Ag bead heated in an alumina crucible and no annealing procedure was applied to the overlayer. The amount of deposited Ag was determined by means of a calibrated quartz microbalance. Two Cu(001) crystals were employed for the ARPES and STM experiments and identical Ag evaporators were mounted at the same distance from the sample in all the experimental chambers to ensure the same amount of deposited Ag observed in STM and (AR)PES experiments. ARPES data were acquired with $k_{\parallel}$ varying along the ⟨100⟩ and ⟨110⟩ azimuthal direction.

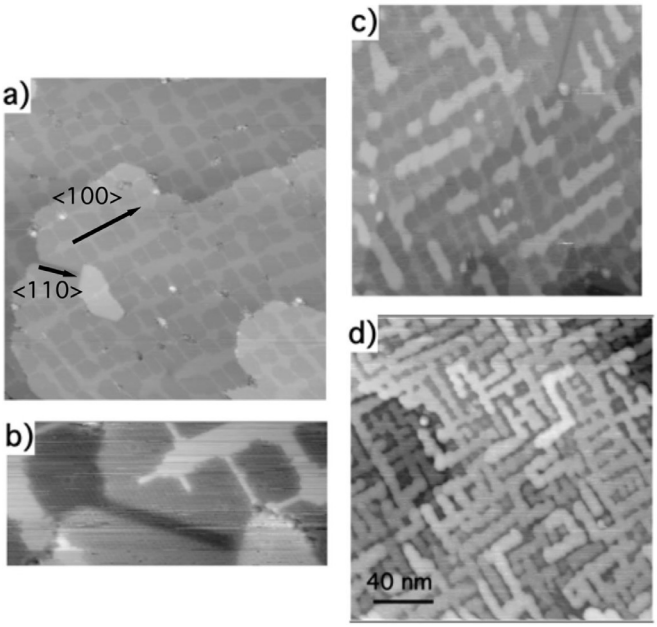

Fig. 1. (a) and (b) 0.25 ML of c(2 × 2)-N/Cu(001). The N covered parts appear as depressions. The N islands are about 5 × 5 nm^2. (c) 0.25 ML of c(2 × 2)-N/Cu(001) plus 0.1 ML of Ag (showing as striped protrusions). (d) 0.25 ML of c (2 × 2)-N/Cu(001) and 0.5 ML of Ag. Small, but high and round protrusions appearing occasionally on 1 (a), (c) and (d) which are due to the tip.

3. Results and discussion

3.1. STM results

Fig. 1a-b shows some examples of STM images from the N precovered surface. Our images are similar to the ones obtained in previous studies in which the N growth mode has been described accurately [13,14,22] and here we report some results for the sake of clarity. The N islands appear as depressions in the image. From Fig. 1(a) it can be estimated that the N coverage is about 0.25 ML, i.e. about 50% of the initial surface is made of two domains of c(2 × 2)-N islands arrays and by domains of clean unreconstructed Cu(001) stripes running along the ⟨100⟩ azimuthal direction.. Fig. 1b shows faceting of the island at the island corners and the occasional coalescence of N islands at the junction between domains of N islands with edges terminating along the ⟨110⟩ azimuthal direction. This peculiarity in the N overlayer is rarely found and it is reported here as an example.

Fig. 1(c) and (d) and Fig. 2(a)–(e) report the growth of Ag on the N modified Cu surface, from the very early stage (0.1 ML of Ag) up to coverage values corresponding to a volume of 8 flat Ag monolayers on Cu(001). The growth of Ag on bare Cu(001) has been extensively studied with a number of techniques. In summary, at a thickness of up to 1 ML, the Cu and Ag lattice mismatch determines a growth of Ag in the shape of a quasi hexagonal c(2 × 10) structure [34,35,45,46]. Note that room temperature Cu(001)- Ag alloying, confined to the 2D surface, was predicted for very low Ag coverages ($\Theta_{Ag} < 0.13$ ML) [47]. From the data shown in Fig. 2(c) we cannot give evidence of this process. At